

# Surface Dynamics during Environmental Degradation of Crystal Surfaces

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# **Surface Dynamics during Environmental Degradation of Crystal Surfaces**

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## **Motivation and Purpose**

While a great deal of effort has been invested into understanding the physics and chemistry of environmental attack on metal surfaces, little attention has been given to degradation of dielectric crystalline surfaces used for optical applications. Although it is generally possible to isolate such surfaces in vacuum chambers or purged environments, this is not always the case. In addition, even when nominal isolation from the outside world is possible, contamination either present on the surface as a result of finishing the optic or introduced to the surface within the vacuum environment can lead to surface degradation. This problem may be particularly pronounced when the surface has a porous anti-reflective or high reflective coating that acts like a getter for volatile contaminants. Furthermore, the ever increasing internal quality of these materials and the rising demand of UV applications such as UV photolithography has led to their widespread use in high power UV systems where surface degradation is even more pronounced.

The National Ignition Facility is the quintessential high power UV system. Its successful deployment and operation depends on the ability of a number of optical surfaces to survive high fluence UV environments. Recently, the formation of pits with distinct geometrical features was discovered on the surface of the sol-coated  $\text{KH}_2\text{PO}_4$  (KDP) and  $\text{KD}_2\text{PO}_4$  (DKDP) crystals used for optical switching and frequency conversion on Nova, Omega, and Beamlet after they were coated with anti-reflective coatings. These pits scattered up to 10% of the incident light, resulting in both a loss of energy on target and the potential to produce collateral laser damage through beam modulation and/or contamination from structural material ablated by the scattered light. We have identified these pits as the product of dissolution by water that is adsorbed into the coating. However, the kinetics of pit formation varied dramatically as the surface type was varied from "as-grown" to mechanically finished to thermally annealed or as the sol coating method and chemistry were varied. The purpose of this proposal was to develop a fundamental understanding of the physics and chemistry of the environmental degradation processes at crystal surfaces.

## **Summary**

Using in situ optical microscopy and scattering measurements, we have followed the evolution of surface morphology during etching and measured surface etching rates as a function of humidity and undersaturation. From our experiments to date we have developed the following picture of etch pit formation on KDP crystal surfaces. Pit formation is characterized by a nucleation and growth process: the introduction of water creates a condition of undersaturation at the crystal surface. The equilibrium step directions define the orientation of the edges of the pits and the internal surfaces of the pits are low index facets of KDP. For z-cut and type I crystals, the pits are self-similar, indicating their geometry is controlled by equilibrium, not kinetic parameters. For type II crystals, the aspect ratio of the pits can vary dramatically from sample to sample or even within a sample, showing that the kinetics of dissolution can also play a role in determining overall etch pit geometry. The onset of pit formation during exposure to 55% relative humidity (RH) is detectable within a few hours and most of the etching process is complete within 48 hours, but pits continue to grow for a week or longer. At 75% RH, pits are detectable within minutes. Defects such as scratches promote a locally high density of nucleation sites surrounded by a denuded zone which indicates that the density and size of the resulting etch pits depends on a combination of nucleation probability and the diffusivity of the dissolving species. At 55%

RH, coarsening has not been observed and the etch pit size distribution is monomodal. At 75%, coarsening is often observed after a critical undersaturation value is exceeded, and a bimodal pit size with denuded zones around the preferential growth sites always develops. The total volume of the pits qualitatively scales with coating thickness and relative humidity indicating that the adsorption of water into the porous coating determines the size of the available solvent reservoir.

Subtle modifications of the KDP surface (2,3) or the sol coating chemistry and structure (4) can enhance or retard the growth of etch pits under otherwise similar conditions, resulting in changes in either the number density or total volume of etch pits. Intentional modification of the surface of the porous sol by reaction with hexamethyldisilazane (HMDS) to increase hydrophobicity results in measurable reduction of adsorbed water and can eliminate etch pit growth at 55% RH. Reacting the KDP surface with a zirconium-organo-phosphate coupling agent or thermal annealing at 160°C for one week before coating, strongly inhibits pit formation. Most thermal annealed surfaces show no evidence of dissolution even after months at high humidity. The reduction in etch-pit formation is correlated to the formation of an insoluble dehydrated layer of linear polymeric phosphate on the surface of the KDP. This layer was identified through Fourier Transform Infrared (FT-IR) spectroscopy, electron spectroscopy for chemical analysis (ESCA), x-ray fluorescence (XRF), and x-ray diffraction.

This project focused on developing a fundamental understanding of the physics and chemistry of the environmental degradation processes at crystal surfaces. Successful completion has established a firm scientific basis for robust mitigation strategies and a broader understanding of the physics of surface etching.

## Publications

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